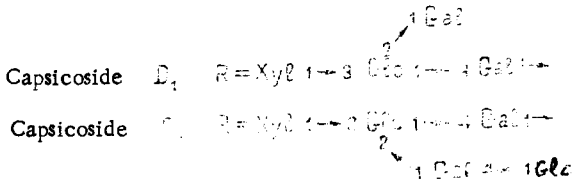


Capsicoside D_1

Capsicoside

The configurations of the glycosidic centers determined from the difference between the molecular rotations of the glycoside and its progenins corresponded to Klyne's rule [5].

Capsicoside D_1 proved to be identical with gitonin [6] isolated previously after the enzymatic hydrolysis of lanotigoside from the leaves of *Digitalis lanata*.

LITERATURE CITED

1. P. K. Kintia [Kintya], E. V. Gutsu, G. V. Lazurievsky, N. N. Balachova, and L. P. Kovalchuk, IInd International Conference on the Chemistry and Biotechnology of Biologically Active Natural Products. Abstracts, Budapest (1983), p. 156.
2. V. V. Krokhmalyuk, P. K. Kintia, and V. Ya. Chirva, Izv. Akad. Nauk MSSR, Ser. Biol. Khim. Nauk, No. 1, 85 (1975).
3. S. Hakomori, J. Biochem. (Tokyo), 55, 205 (1964).
4. T. Kawasaki, I. Nishioka, T. Komori, T. Yamauchi, and K. Miyahara, Tetrahedron, 21, 289 (1965).
5. W. Klyne, Biochem. J., 47, No. 41 (1950).
6. R. Tschesche, S. Lother, Ch. Sh. Satish, and W. Gunter, Chem. Ber., 105, 3397 (1972).

SYNTHETIC ANALOGUES OF *Peganum* ALKALOIDS.

IV. INTRODUCTION OF BROMINE INTO THE BENZENE RING OF QUINAZOLINES. 6-BROMOPEGANINE AND 6-BROMODEOXYPEGANINE

M. V. Telezhenetskaya and A. L. D'yakonov

UDC 547.944/945+547.856.1

The reaction of 4-quinazolones with electrophilic reagents has been studied in fairly great detail [1]: only in the nitration and sulfochlorination reactions does substitution take place in the benzene ring. The substituent then occupies position 6. On the bromination of 2,3-polymethylene-3,4-dihydro-4-quinazolones, no substitution of the benzene ring takes place. Depending on the reaction conditions, perbromides or 9-substituted 4-quinazolines are obtained. Only one reaction has been described for the quinazolone series — nitration [2], in which the nitro group likewise occupies position 6.

We have performed the bromination of the quinazoline alkaloids peganine (Ia) and deoxypeganine (Ib) with bromosuccinimide in glacial acetic acid. The yields of the bromination products (IIa and b) amounted to 50-70%.

Compound (IIa), mp 206°C (decomp.), $[\alpha]_D$ − 97° (c 1.2; chloroform); absorption bands in the UV spectrum of (IIa) (229, 310 nm) showed retention of the quinazoline skeleton, and M^+ 266/268 the fact that a monobromo derivative had been obtained.

Signals in the PMR spectrum ($CDCl_3$, δ, ppm) of product IIa at 4.50 (2H, s), 4.57 (1H, m), 2.15 (2H, m), and 3.20 (2H, m) must be assigned to the protons in positions 4, 9, 10, and 11, respectively. Consequently, the bromine cannot have entered rings B or C. Substitution took place in the benzene ring, A. Judging from the nature of the splitting of the signals of the aromatic protons (6.94, d, J = 3 Hz; 7.17 dd, J = 9.5 Hz, J = 3 Hz; and 6.84, d, J = 9.5 Hz), substitution took place in positions 6 and 7. The choice was made on the basis of the results of a study of a minor product of this reaction.

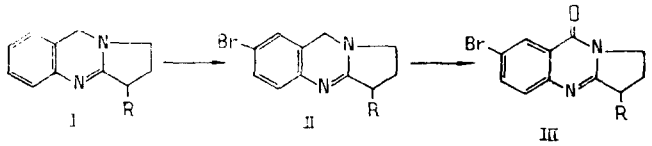
Institute of the Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR, Tashkent.

Translated from Khimiya Prirodnykh Soedinenii, No. 2, pp. 309-310. Original article submitted November 14, 1986.

0009-3130/87/2302-0261$12.50

Compound (III) gave three absorption bands in the UV spectrum — 275, 312, 325 nm, which are characteristic for quinazolines — while the IR spectrum had the band of an amide carbonyl at 1680 cm^{-1}. The molecular weight of (III) was 280/282. These facts enable compound (III) to be identified as bromovasicinone.

The PMR spectrum of (III) had the signals of the protons of ring C and of three aromatic protons: 8.18 d, J_{meta} = 1.5 Hz; 7.77 dd, J_{meta} = 1.5 Hz, J_{ortho} = 9 Hz; and 7.32 d, J_{ortho} = 9 Hz. A weak-field signal at 8.18 ppm must be assigned to a proton present in the peri-position with respect to the carbonyl group, i.e., to the proton at C-5. The meta-splitting of the signal of the proton at C-5 was possible only if position 6 had been substituted by bromine. Consequently, the transformations in this reaction were as follows: peganine (I) → bromopeganine (II) → bromovasicinone (III), which enables the position of the bromine to be determined as C-6 in bromopeganine, (II), as well. The possibility that peganine is first oxidized to vasicinone and is then brominated to bromovasicinone is excluded on the basis of the fact that, according to our own observations and literature information, quinazolones are not brominated in the benzene ring under similar conditions.



I, II, III, a: R=OH; b: R = H

From deoxypeganine (Ib) under similar conditions we obtained 6-bromodeoxypeganine (IIb), mp 181-182°C, hydrobromide, mp 286-288°C (decomp.), λ_{max} 227, 302 nm, M^+ 250/252, PMR ($CDCl_3$): 6.87 (1H, d, J_{meta} = 1.5 Hz, C-5); 7.15 (1H, d, J_{ortho} = 9 Hz, J_{meta} = 1.5 Hz, C-7); 6.77 (1 H, d, J_{ortho} = 9 Hz; C-8); 4.33 (2 H, s, C-4); 2.50 (2 H, m, C-9); 1.95 (2 H, m, C-10); and 3.15 (2H, t, C-11).

LITERATURE CITED

1. É. Oripov, Kh. M. Shakhidoyatov, Ch. Sh. Kadyrov, and N. D. Abdullaev, Khim. Prir. Soedin., 684 (1979).
2. T. Williamson, The Chemistry of Quinazoline, in: Heterocyclic Compounds [Russian translation], Moscow (1960), p. 268.
3. M. P. Jain, C. K. Atai, R. Randhyopadhyay, and B. Nacavi, Indian J. Pharm. Soc., 45, 178 (1983).